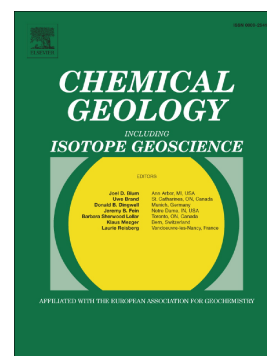


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A new all-metal induction furnace for  
noble gas extraction

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## Abstract

A new all-metal induction furnace for extraction of all noble gases from pyroxenes, olivines, quartz or barites has been developed at CRPG. It differs in design from other induction furnaces in that the totality of the vacuum vessel is metallic and the induction coil, normally located outside the furnace, has been placed inside the vacuum vessel, with a special radio frequency power feedthrough welded onto a flange. The volume of the crucible is  $\approx 15 \text{ cm}^3$  and permits fusion of samples with a mass of up to 1 g. Samples are packed into a metal foil, loaded into a carousel, baked out before analysis, and then sequentially dropped into the Ta-

crucible. The low weight of the crucible ( $\approx 120$  g) allows for short and efficient degassing cycles. When the furnace is pumped for the first time after samples loading, short cycles between 500 and 1800°C at fast heating rates ( $\approx 400^\circ\text{C}\cdot\text{min}^{-1}$ ) are sufficient to achieve very low blanks. The durations of these cycles are range from 30 minutes for He to up to a few hours for Ne, Kr and Xe. Blanks of He, Kr and Xe (10 min. heating durations) and Ne (20 min.) in static vacuum are  $(1.6 \pm 1.0) \times 10^{-15}$  mol  $^4\text{He}$  ( $T=1750^\circ\text{C}$ ),  $(5.8 \pm 2.3) \times 10^{-17}$  mol  $^{20}\text{Ne}$  ( $T=1500^\circ\text{C}$ ),  $(2.1 \pm 0.3) \times 10^{-18}$  mol  $^{84}\text{Kr}$  ( $T=1700^\circ\text{C}$ ) and  $(4.4 \pm 0.4) \times 10^{-18}$  mol  $^{132}\text{Xe}$  ( $T=1700^\circ\text{C}$ ). Argon blanks have not yet been measured.

## 1 Introduction

In most laboratories, noble gases are extracted from rocks and minerals using double vacuum resistance furnaces (e.g. Blard et al., 2015; Niedermann et al., 1997; Maruoka and Matsuda, 2001), simple vacuum furnaces (e.g. Burgess et al., 2009; Honda et al., 1987; Zimmermann et al., 2012), glass induction furnaces (e.g. Marty et al., 1995; Moreira and Allègre, 2002; Ott, 1988) or lasers (e.g. Farley et al., 2006; Füre et al., 2015; Stuart et al., 1999). However, these methods, although effective, have several limitations:

i) Double vacuum resistance furnaces use an electrical resistance to heat a Ta or Mo liner inside a Ta tube (Staudacher et al., 1978; Takaoka, 1976). Extraction temperatures of up to 1800°C can be achieved, resulting in blanks in the ranges of  $1.7 \times 10^{-16}$  to  $7.5 \times 10^{-14}$  mol  $^4\text{He}$ ,  $1.3 \times 10^{-16}$  to  $2.7 \times 10^{-15}$  mol  $^{20}\text{Ne}$ ,  $1.3 \times 10^{-17}$  to  $5.1 \times 10^{-17}$  mol  $^{84}\text{K}$  and  $0.2 \times 10^{-17}$  to  $0.2 \times 10^{-16}$  mol  $^{132}\text{Xe}$  (Supplementary information, table 1). Lavielle et al. (1999) describe also a similar double-walled vacuum furnace with which high temperatures ( $\approx 2000^\circ\text{C}$ ) are achieved via electron bombardment onto a

Ta crucible. Their helium and neon blanks are also very low at  $1.8 \times 10^{-15}$  mol  $^4\text{He}$  and  $0.4 \times 10^{-17}$  mol  $^{20}\text{Ne}$  respectively (Supplementary information, table 1). This technology has thus rather good analytical performances, but it also has several drawbacks that may degrade the quality of the gas extractions. First, the heating cycle for samples is long because of the need to maintain slow heating and cooling rates ( $< 100^\circ\text{C}.\text{min}^{-1}$ ) in order to protect the heating components against electrical and thermal stress. Furthermore, the Ta-tube is heavy (0.7 to 1 kg), resulting in a significant thermal inertia. Thus, the temperature increase and decrease steps are typically about 20 minutes in duration, which may result in high noble gas blanks. Second, this technology is costly requiring expensive electrical resistances and thermal shields, a turbomolecular pumping system connected to the double vacuum vessel, and frequent replacement of the tantalum crucible after melting of samples ( $\approx 1500$  €/crucible). Third, noble gases extracted from samples may be pumped out by the external pumping system through cracks produced by recrystallisation of the crucible walls after several heating cycles.

ii) Simple vacuum resistance furnaces (Burgess et al., 2009; Honda et al., 1987; Sumino et al., 2011) have been developed to avoid loss of gas through the crucible wall. The large resistance, the Ta-crucible and the double vacuum vessel used in the double vacuum furnaces have been replaced by a W or Ta coil fixed into a single vacuum vessel, and heated by Joule effect to up to  $2100^\circ\text{C}$ . The use of this type of furnace is limited to small samples ( $< 100$  mg), because the inner volume of the coil is low, typically  $< 0.5$  cm<sup>3</sup>. In addition, samples must remain in a solid state (without melting) during the extraction in order to avoid being lost through the coil wires. Zimmermann et al. (2012) developed an alternative design for a simple vacuum resistance furnace, in which the metal coil used by Honda et al. (1987) was

replaced by a Ta-resistance wrapped around a boron nitride (BN) crucible. This furnace yields satisfactory helium and neon blanks (Supplementary information, table 1), but not capable of melting refractory samples such as high-Mg olivines because the temperature is limited to 1450°C. Furthermore, BN degasses large amounts of nitrogen ( $> 10^{-2}$  mbar) at high temperatures, which necessitates a long and thorough purification procedure. Finally, the low heating rate, of around 70°C.min<sup>-1</sup>, (recommended to extend the life of the resistance) tends to increase the noble gas blanks.

iii) Farley et al. (1999) described a helium diffusion system developed specifically for He analyses, in which samples are heated by radiation using a halogen lamp (250 W). The He blanks are remarkably low (1.0 to 4.0 x10<sup>-15</sup> mol <sup>4</sup>He at 750°C), but a maximum temperature of 1000°C limits the use of this system to He diffusion experiments.

iv) Induction furnaces using a glass vacuum vessel are also used to extract noble gases. Crucibles are heated by an external induction coil and the glass walls are cooled by water circulation. High temperatures of up to 1800°C can be reached, allowing extraction of noble gases from refractory samples such as olivine or barite (e.g. Avce et al., 2015; Becker and Pepin, 1984; Marty et al., 1995; Moreira and Allègre, 2002; Ott, 1988), and the Ne, Kr and Xe blanks are similar to or lower than those of all-metal furnaces (Supplementary information, Table 1). However, despite these advantages, the use of these furnaces is often challenging because (a) the heating rate required to reach high temperatures must be low ( $< 50^{\circ}\text{C}.\text{min}^{-1}$ ) in order to minimize thermal stress on the quartz crucible holder, (b) the volume of the crucible is low ( $< 3\text{ cm}^3$ ), and (c) the helium blanks are high, generally  $> 9 \times 10^{-14}$  mol

$^4\text{He}$  ( $T > 1500^\circ\text{C}$ ) (Supplementary information, table 1) due to He diffusion through the pyrex or through the kovar vacuum envelope.

v) Laser systems ( $\text{CO}_2$ , Nd-Yag, Diode) are also used to heat/melt mineral grains. These have the advantage of being able to rapidly reach high temperatures in excess of  $1600^\circ\text{C}$  if necessary. Laser systems also yield low blanks (Supplementary information, table 1) as the vacuum vessel walls and the sample holders are heated only moderately since most of the laser energy is transmitted to the samples. However, the low power and small diameters of the beams ( $\approx 100\text{-}200\ \mu\text{m}$ ) limit these systems to small sample sizes, typically below 10 mg. Further complications may arise from vapor deposition on the laser chamber windows, or degradation of the latter by the laser beam.

In this contribution, we describe a new ultra-high vacuum all-metal induction furnace, which has been designed, built and tested at CRPG (Nancy, France). A Ta crucible and an induction coil are placed inside an all-metal vessel that can be pumped at high vacuum. The crucible easily reaches high temperatures ( $\approx 1800^\circ\text{C}$ ) unlike the furnaces described by Farley et al. (1999) and Zimmermann et al. (2012), which are limited to  $1450^\circ\text{C}$  and  $1000^\circ\text{C}$ , respectively. This allows the extraction of more than 99% of the noble gases contained in minerals such as quartz, pyroxene, olivine, barite or sulfide. Unlike laser systems (e.g. Füri et al., 2015) or other simple vacuum furnaces that have been described (e.g. Honda et al., 1987), up to 1 g of rock/mineral sample can be melted in the large crucible. The vacuum vessel is not permeable to He, in contrast with glass induction furnaces (Marty et al., 1995), and its design prevents gas loss, a problem encountered with double-vacuum resistance furnaces. Finally, the crucible/furnace tolerate severe temperature variations ( $> 400^\circ\text{C}\cdot\text{min}^{-1}$ ) allowing the heating and the cooling cycles to be optimized and the

noble gas blanks to be reduced to  $(1.6 \pm 1.0) \times 10^{-15}$  mol  $^4\text{He}$  ( $T=1750^\circ\text{C}$  for 10 min.),  $(5.8 \pm 2.3) \times 10^{-17}$  mol  $^{20}\text{Ne}$  ( $T=1500^\circ\text{C}$  for 20 min.),  $(2.1 \pm 0.3) \times 10^{-18}$  mol  $^{84}\text{Kr}$  ( $T=1700^\circ\text{C}$  for 10 min.) and  $(4.4 \pm 0.4) \times 10^{-18}$  mol  $^{132}\text{Xe}$  ( $T=1700^\circ\text{C}$  for 10 min.).

## 2 Description of the furnace

### 2.1 Design of the vacuum vessel

The vacuum chamber of the furnace is made of stainless steel (304L and 316LN). It is mainly composed of two CF160 flanges. A CF40 flange welded onto the upper part allows the vacuum vessel to be connected to a carousel that hosts the different samples (not shown in Figure 1) and to the purification line. A pyrex viewport is also connected to the carousel so that the temperature of the crucible can be monitored with an optical pyrometer (Impact<sup>®</sup>, pyrometer IS-2). A funnel has been machined into the upper CF160 flange to guide the samples toward the Ta crucible after they have been dropped. The upper flange is cooled by water circulation (Inner cooling N°1, Figure 1). A double wall is welded onto the inside of the lower CF160 flange to cool the lateral surface of the furnace (Inner cooling N°2, Figure 1) and finally, a third water circulation system is welded onto this double wall in order to cool the entire lower surface of the vessel (Inner cooling N°3, Figure 1).

A 15 cm<sup>3</sup> crucible, containing the samples and made of tantalum (Neyco Company<sup>®</sup>), is heated by induction. The crucible is maintained in the middle of the vacuum vessel by a ceramic holder (Figure 1). This ceramic is only slightly affected by the severe variations in the crucible temperature.

All condensable species, such as Al and Sn from the metallic foils or carbon, chlorides and sulphides released upon heating of the minerals, are condensed on a quartz cylinder placed around the crucible. This minimizes fouling of the inner surface of the furnace and protects the induction coil against short circuits (Figure 2).

The induction coil is positioned around the quartz tube and is connected to a high frequency (HF) electrical feedthrough cooled by water circulation. The coil has been adapted to fit the geometry of the tantalum crucible in order to optimize the heating.

The size of the vacuum vessel was designed to avoid over-heating of the walls by the coil. The volume of the furnace ( $\approx 2100 \text{ cm}^3$ ) is large compared to that of the purification line ( $\approx 800 \text{ cm}^3$ ). The use of a cryogenic trap is therefore strongly recommended so that the noble gases can be focused into a smaller volume outside the furnace, thereby allowing the signal of the sample to be optimized for analysis by the mass spectrometer.

The inner surface of the furnace was initially cleaned in three ultrasonic baths, for 2-3 hours each time, in diluted Decon90, a detergent used to eliminate up to 99.95% of hydrocarbons present on the metallic surfaces (Chiggiato et al., 1999). After each bath, the furnace was systematically rinsed with deionized water. Finally, the furnace was dried in an oven at 100-110°C before its first use.

During extraction, two fans are used to cool the HF electrical feedthrough welded onto a CF63 flange. A triple water cooling system ( $\approx 60 \text{ l.h}^{-1}$ ) that passes through the upper CF160 flange, the vertical wall of the vessel and the base of the furnace, is used to cool the inner surface (Figure 3). The external temperature of the furnace, measured at points A, B, and C (Figure 1), remains below 30°C after heating



the crucible at 1800°C for 20 minutes. The temperature of the CF63 flange can reach 50°C (point D, Figure 1).

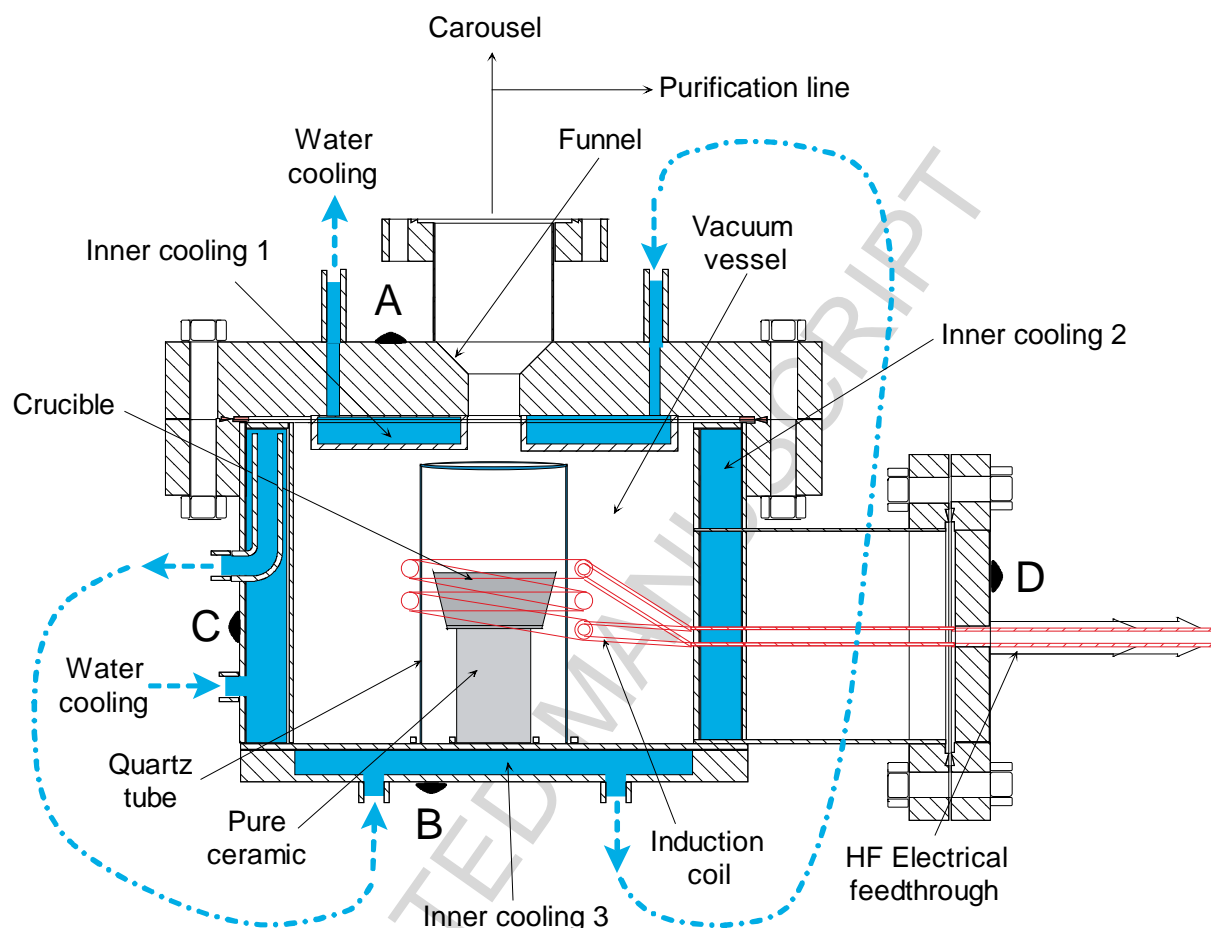


Figure 1: Schematic diagram of the all-metal induction furnace showing the induction coil with the tantalum crucible, the ceramic crucible holder, the quartz tube and the triple water circulation system (Inner cooling circuits 1, 2 and 3) used to cool the inner surface of the vacuum vessel. The pyrex viewport, not shown, is located on a CF40 flange at the top of the carousel. Temperature measurements were made outside the vacuum vessel (points A, B, C and D) using a K-type thermocouple.

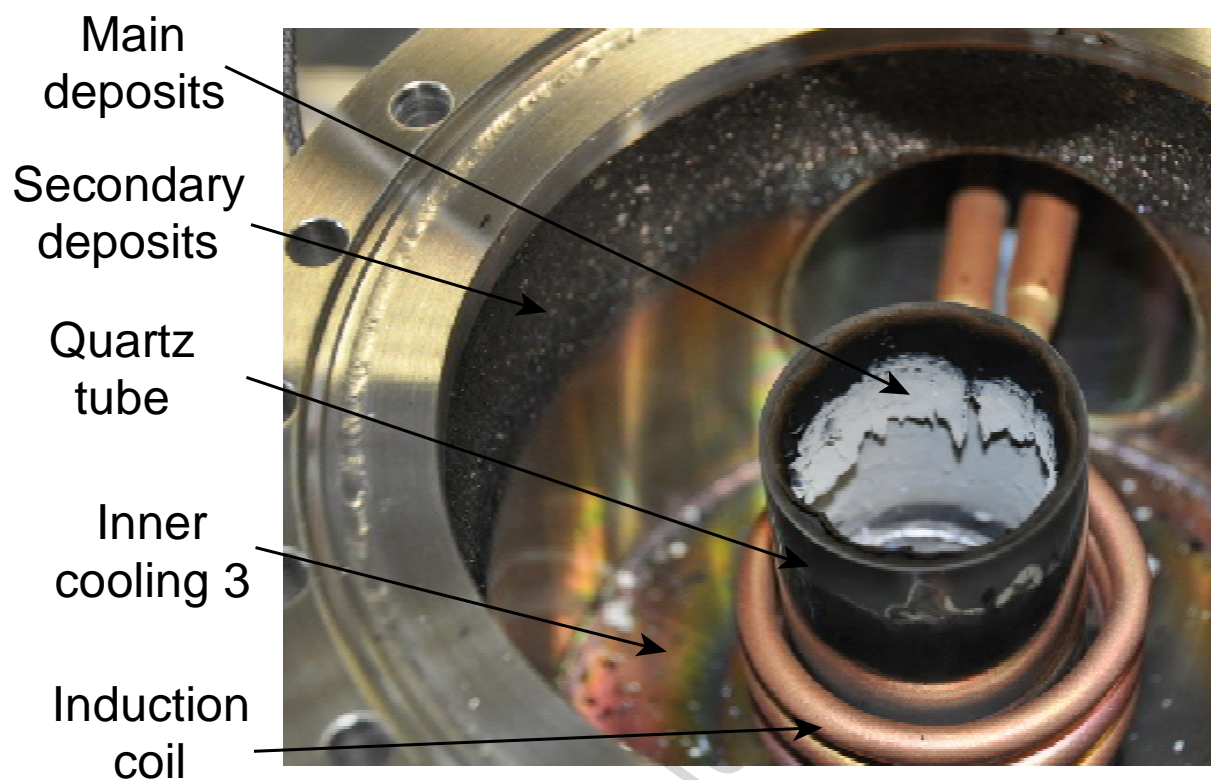


Figure 2: Close-up of the bottom part of the furnace. The distance between the top of the quartz tube and the top of the CF160 flange has been reduced to  $< 2$  mm in order to favour deposition of any carbon, sulphide and chlorides complexes on the inner surface of the quartz tube. Secondary deposits can be observed on the upper part of the double wall. These represent less than 5 wt. % of the total deposits.

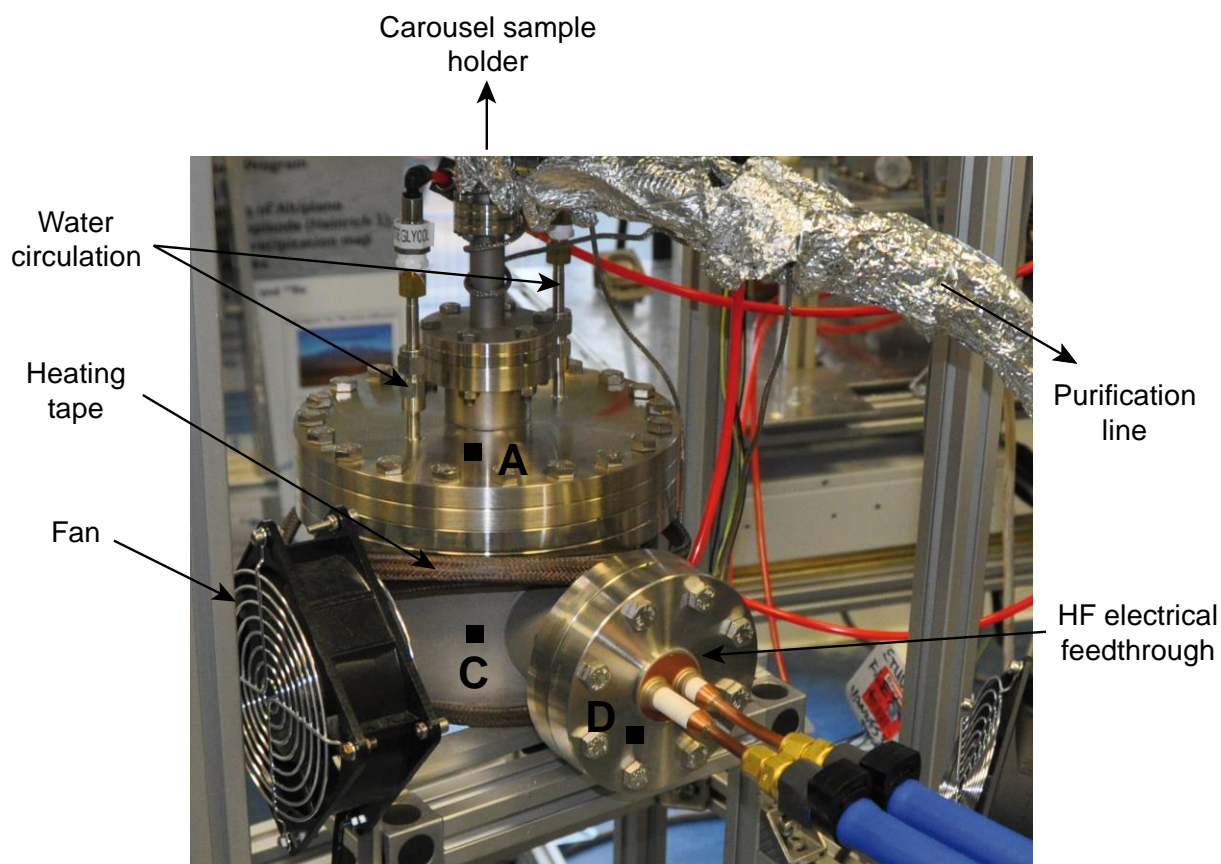


Figure 3: External view of the all-metal induction furnace. A heating tape wrapped around the vacuum vessel is used to bake the furnace at up to 200°C in order to desorb atmospheric gases from the inner surfaces. After one night of baking under vacuum, the pressure ( $\approx 5.0 \times 10^{-9}$  mbar) is compatible with the requirements for noble gas measurements. Three water circulation systems, connected by red plastic tubes, cool the inner walls during an extraction. To check the efficiency of the furnace cooling, temperatures were measured at points A, C, and D.

## 2.2 Materials

The choice of materials used for the different components is critical to ensure good thermal, electrical, and mechanical properties, to prevent any contamination (e.g., by chemicals or manufacturing residues), and to ensure low noble gas blanks.

Tantalum was chosen for the crucible for two main reasons:

- i) This metal allows very low noble gas levels to be achieved. Helium blanks determined during preliminary tests performed at 1500°C for 10 minutes were  $9.0 \times 10^{-15}$  mol  $^4\text{He}$ . Similar tests, with a Mo crucible, yielded  $^4\text{He}$  blanks that were one order of magnitude higher. For krypton and xenon, the blanks obtained for 30 minutes heating at a temperature of 1500°C were  $1.3 \times 10^{-17}$  mol  $^{84}\text{Kr}$  and  $2.2 \times 10^{-18}$  mol  $^{132}\text{Xe}$ , respectively (Honda et al., 1993).
- ii) With a melting temperature of 3020°C, tantalum also has the advantage of being refractory, meaning that it is able to withstand the highest temperatures ( $\approx 1800^\circ\text{C}$ ) obtainable by this furnace.

Preliminary tests revealed very high Ar blanks ( $\geq 10^{-10}$  mol  $^{40}\text{Ar}$ ) at 1700°C with an isotopic composition similar to that of air. This contamination is likely due to the fact that the crucible, was manufactured under which an argon atmosphere to avoid oxidation of tantalum at high temperature. We are currently exploring other commercial suppliers to resolve this issue. Ar blanks are thus not discussed further in the sections that follow.

The crucible sits on an ultra-pure ceramic ( $\text{Al}_2\text{O}_3$ ) base. This material offers three main advantages:

- i) it is refractory ( $t_{\text{melt}} = 2030^\circ\text{C}$ ),
- ii) it can tolerate severe temperature variations ( $> 400^\circ\text{C} \cdot \text{min}^{-1}$ ) without damage,
- iii) the noble gas degassing rate of this material at high temperature is low. The physical integrity of the crucible is inspected at each opening of the furnace.

### 2.3 Furnace cleaning operations

We recommend cleaning the furnace after analysis of 20-30 samples in order to remove condensates from the inner surfaces of the furnace. Around 90% to 95% to the condensates are usually present on the inner surfaces of the quartz cylinder. This inexpensive component is systematically replaced at each cleaning operation. Secondary deposits observed on the top upper part of the furnace (Figure 2), representing less than 5 % by mass of the condensed species, are eliminated by suction.

We should emphasize that the state of the crucible may be altered due to chemical reactions between the Ta and the melted minerals (olivines and pyroxenes) at high temperature. We therefore recommend microscopic inspection of the crucible after each opening of the furnace and replacement of the crucible after 50 heating cycles.

### 2.4/ Thermal properties

The temperature of the tantalum crucible was measured through a pyrex viewport using an optical pyrometer (Impac<sup>®</sup>, pyrometer IS-2) and a precise calibration curve between the temperature of the crucible (900°C to 1900°C) and the power settings of the HF generator was established (Figure 4). The accuracy of the temperature measurements was verified by melting two pure metals: Cu foil (1060°C) and Ni foil (1430°C). Temperature was not measured in the 580-900°C range but the

crucible had a reddish glow and the temperatures were estimated from the calibration curve, which tends to be more linear in the lower part of the temperature range.

The heating tests revealed that the tantalum crucible could be heated to up to 1800°C, comparable with the high temperatures ( $> 1500^{\circ}\text{C}$ ) that can be obtained with other induction furnaces (Chennaoui-Aoudjehane, 1992; Marty et al., 1995). The heating rate of  $\approx 400^{\circ}\text{C}.\text{min}^{-1}$  is 5 to 10 times faster than rates obtained with other double-vacuum high temperature furnaces (Aciego et al., 2007; Maruoka and Matsuda, 2001; Staudacher et al., 1978). The cooling rate is also fast (close to  $300^{\circ}\text{C}.\text{min}^{-1}$  for  $\approx 1500^{\circ}\text{C}$  to  $< 500^{\circ}\text{C}$  temperature steps) due to the low thermal inertia of the 120 g crucible. These technical characteristics allow the duration of the heating to be reduced, thereby minimizing the noble gas blanks as well as reducing the amount of  $\text{H}_2$  produced upon heating. Finally, the thermal stability of the furnace at  $\pm 1\%$  (Figure 5) indicates that there is a good balance between the energy input by the crucible induction and the thermal loss by radiation and/or by conduction with the ceramic base.

The induction coil has been adapted to fit the geometry of the tantalum crucible in order to increase the efficiency of the heating so that the thermal loss by conduction is minimized due to the low thermal conductivity ( $\approx 3\text{-}5 \text{ W}.\text{m}^{-1}.\text{K}^{-1}$  at  $1000^{\circ}\text{C}$ ) of the ceramic that supports the crucible.

Table 1 compares the main technical characteristics of this new induction furnace with those of other vacuum furnaces.

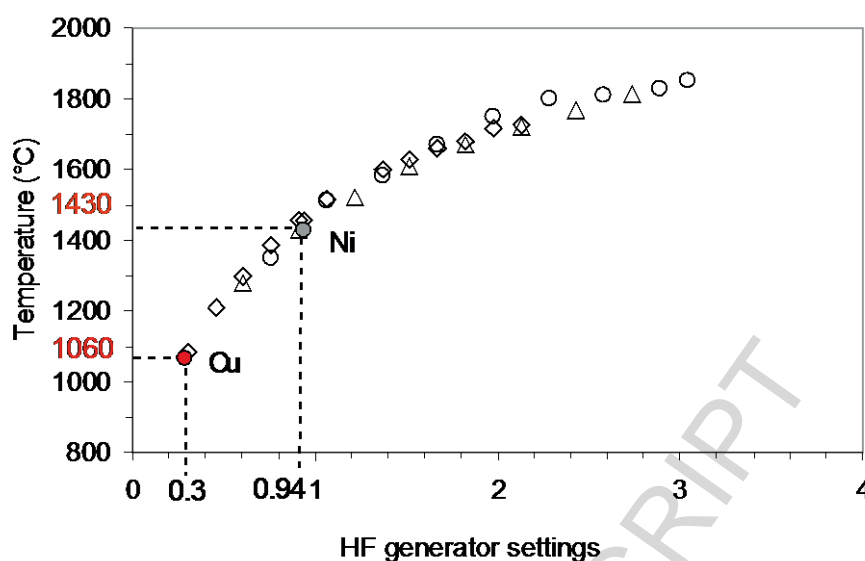


Figure 4: Evolution of the temperature (°C) as a function of the HF generator settings between 1000°C and 1800°C. Five minutes between each temperature step were necessary to ensure temperature stability. The tests were conducted three times (open triangles, circles, and diamonds) and show good reproducibility. The red and grey circles show the melting temperatures of Cu and Ni. At temperatures above 1500°C, thermal losses by radiation reduce the heating efficiency. The induction furnace has been tested up to 1850°C with the HF generator adjusted to 80% of its maximum power.

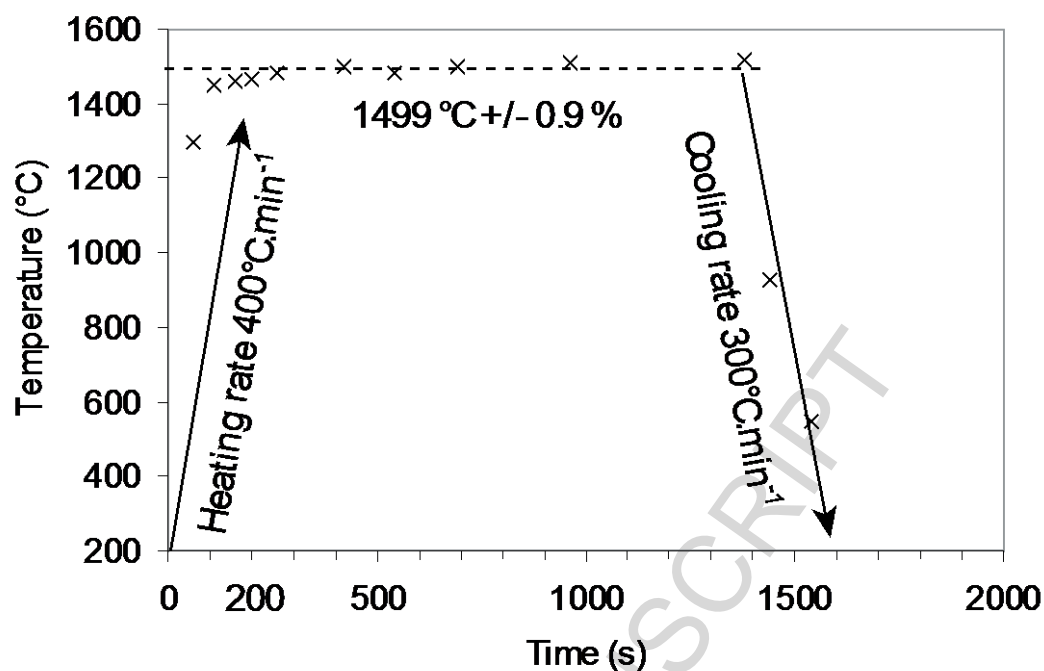


Figure 5: Evolution of the temperature as a function of time. After 200 s, the temperature is stable within  $< 1^{\circ}\text{C}$ , here  $1499^{\circ}\text{C} \pm 0.9\%$ . The heating and cooling rates are  $400^{\circ}\text{C}.\text{min}^{-1}$ . and  $\approx 300^{\circ}\text{C}.\text{min}^{-1}$ , respectively.



	Heating rate (°C.min <sup>-1</sup> )	Cooling rate (°C.min <sup>-1</sup> )	Temp. (°C)	Mass	Vol. (cm <sup>3</sup> ) (crucible)	Vol. (cm <sup>3</sup> ) (vacuum vessel)	Analysis	Carousel	Analytical remarks
[1]	≤ 50	≈ 50	≥ 1800	up to 1 g	≤ 3	≈ 300	He-Xe	Yes	- He diffusion through the vessel glass yields elevated helium blanks
[2]	≤ 100	≈ 100	≈ 1800	up to 1 g	≥ 15	≈ 200	He-Xe	Yes	- Possible loss of gas pumped by the external pumping system
[3]	≈ 70	≈ 70	≤ 1450	up to 1 g	9	≈ 1200	He-Ne	Yes	- The resistance life is limited to 30-40 heating cycles - High nitrogen pressure during extraction
[4]	≥ 1500	≥ 1500	≥ 2000	≤ 100 mg	≤ 0.5	≈ 200	He-Xe	No	- Limited to 4 samples by furnace - Samples can be lost by dropping through the coil wire when melted - Blanks and samples are not analysed in the same analytical session
[5]	≥ 1000	≥ 1000	≥ 1600	≤ 10 mg	-	20-150	He-Ne-Ar	Yes	- Limited to small sample sizes - Vapor deposition on the window
[6]	-	-	≈ 1000	≤ 200 mg	-	200	He	No	- Limited to diffusion experiments - Samples are not melted, leaving the possibility of incomplete extraction of gases
[7]	400	300	1800	up to 1 g	15	2100	He-Xe	Yes	- The power needs to be monitored in order to protect the HF electrical feedthrough

Table 1 : Main technical characteristics of available noble gas extraction systems.

[1] Glass induction furnace (e.g. Marty et al., 1995; Moreira and Allègre, 2002)

[2] Double vacuum furnace (e.g. Maruoka and Matsuda, 2001; Niedermann et al., 1997)

[3] Simple vacuum furnace (e.g. Zimmermann et al., 2012)

[4] Simple vacuum furnace (e.g. Honda et al., 1987; Sumino et al., 2011)

[5] Laser (e.g. Füre et al., 2013; Nichols et al., 1994)

[6] IR Lamp (e.g. Farley et al., 1999)

[7] This study

### 3 Furnace blanks

After baking of the furnace for 12 hours at 200°C, the main source of the noble gas blanks in the furnace is gas atoms adsorbed on the surface of the crucible, especially in the high temperature range above 1500°C. To reduce this contamination, a series of degassing cycles at 1800-1850°C under pumping are carried out. A large amount of neon ( $> 1.0 \times 10^{-14}$  mol  $^{20}\text{Ne}$ ), for example, is degassed from the crucible and the hot ceramic base during the first two cycles, at around 1800°C. The blanks were decreased by a factor of 40 and stabilized at a low and acceptable level of  $\approx 5.0 \times 10^{-17}$  mol after two additional cycles at the same temperature.

The number and duration of these degassing cycles depend on which noble gases are targeted: only 1 cycle of 30 minutes is required for He whereas 3-4 cycles of 60 minutes are required for Ne, Kr and Xe.

The helium blank levels, measured with the furnace closed in static vacuum for 10 minutes are  $(1.8 \pm 1.6) \times 10^{-16}$  mol  $^4\text{He}$  (n=5) at low temperature (1500°C) and  $(1.6 \pm 1.0) \times 10^{-15}$  mol  $^4\text{He}$  (n=18) at 1750°C. These levels are several orders of magnitude lower than those of glass induction furnaces, and are comparable to the lowest blanks obtained with double vacuum furnaces (e.g. Blard et al., 2015; Kurz, 1986; Williams et al., 2005), simple vacuum furnaces (e.g. Blard et al., 2006; Sumino et al., 2011) and lasers (Ammon et al., 2009; Fűri et al., 2013; Stuart et al., 1999).

The variability of helium blanks was tested over a period of one month. Despite periodic exposure of the furnace to the atmosphere for sample loading or

analyses of gas-rich sample extractions ( $^4\text{He} > 1.0 \times 10^{-12}$  mol), the blanks varied by no more than 50-70% (Figure 6) and at no time did we observe any memory effect of this gas in the furnace.

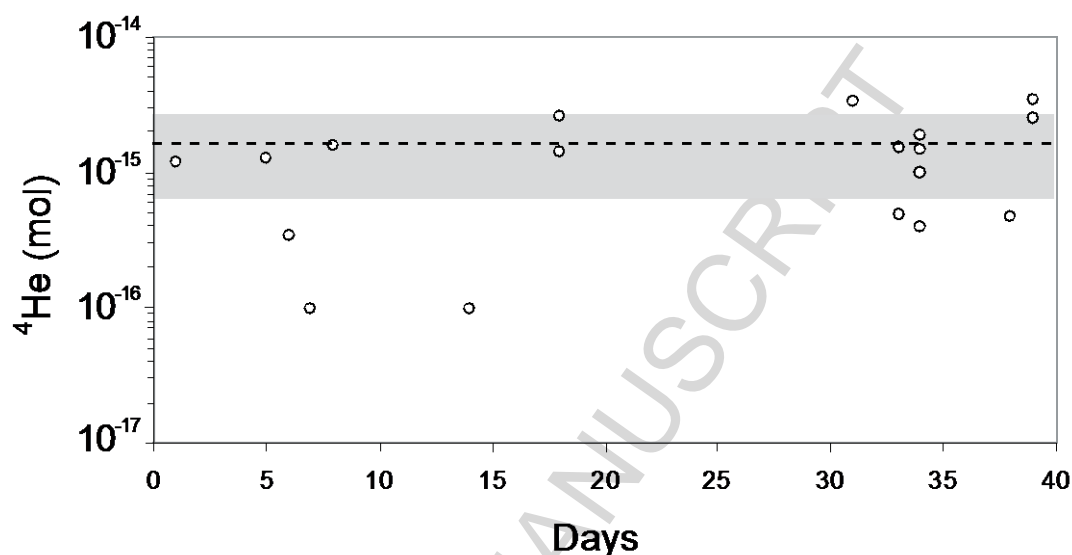


Figure 6: Variation in procedural  $^4\text{He}$  blanks over a period of 40 days. The dashed line represents the mean value ( $1.6 \times 10^{-15}$  mol  $^4\text{He}$ ) and the grey band indicates deviations of 50% relative to the mean value. This variability is comparable for the other noble gases. Part of the He blank might also be derived from helium diffusion through the pyrex viewport connected to the upper CF160 flange.

The neon blanks for 20 minutes at extraction temperature were  $(5.8 \pm 2.3) \times 10^{-17}$  mol  $^{20}\text{Ne}$  (n=7) at 1500°C and  $(1.6 \pm 0.5) \times 10^{-16}$  mol  $^{20}\text{Ne}$  (n=6) at 1600-1700°C. Lavielle et al. (1999) and Sumino et al. (2011) report blanks lower than  $1.0 \times 10^{-17}$  mol  $^{20}\text{Ne}$ . This is probably because these furnaces are degassed at 2000°C in order to optimize the degassing of the tantalum tube. Neon blanks of laser chambers may also reach  $1.0 \times 10^{-17}$  mol (Nichols et al., 1994), thanks to the small inner volumes of

these devices. Finally, at temperatures lower than 1200°C, the neon blanks are similar to those of the whole purification line ( $\approx 2.5 \times 10^{-17}$  mol  $^{20}\text{Ne}$ ).

$^{84}\text{Kr}$  blanks are  $(2.6 \pm 0.3) \times 10^{-19}$  mol at 800°C and  $(2.1 \pm 0.3) \times 10^{-18}$  mol at 1700°C, for 10 minutes' heating. The  $^{132}\text{Xe}$  blanks at 1700°C are  $(4.4 \pm 0.4) \times 10^{-18}$  mol for the same heating duration.

Most samples are packed in metallic foil before melting in the crucible. This packaging is ideal for analysis of samples with a small grain size (< 500 microns), but Niedermann et al. (1997) suggest that chemical reactions between the metallic foil and the Ta crucible might increase noble gas blanks during heating. In agreement with this observation, the heavy noble gas blanks measured here were systematically seven times greater for  $^{84}\text{Kr}$  ( $\approx 1.5 \times 10^{-17}$  mol) and three times greater for  $^{132}\text{Xe}$  ( $\approx 1.4 \times 10^{-17}$  mol) when metallic foil was melted in the crucible.

Helium and neon blank levels, as detected after melting of metallic foil are generally similar to those measured without Sn or Al foil.

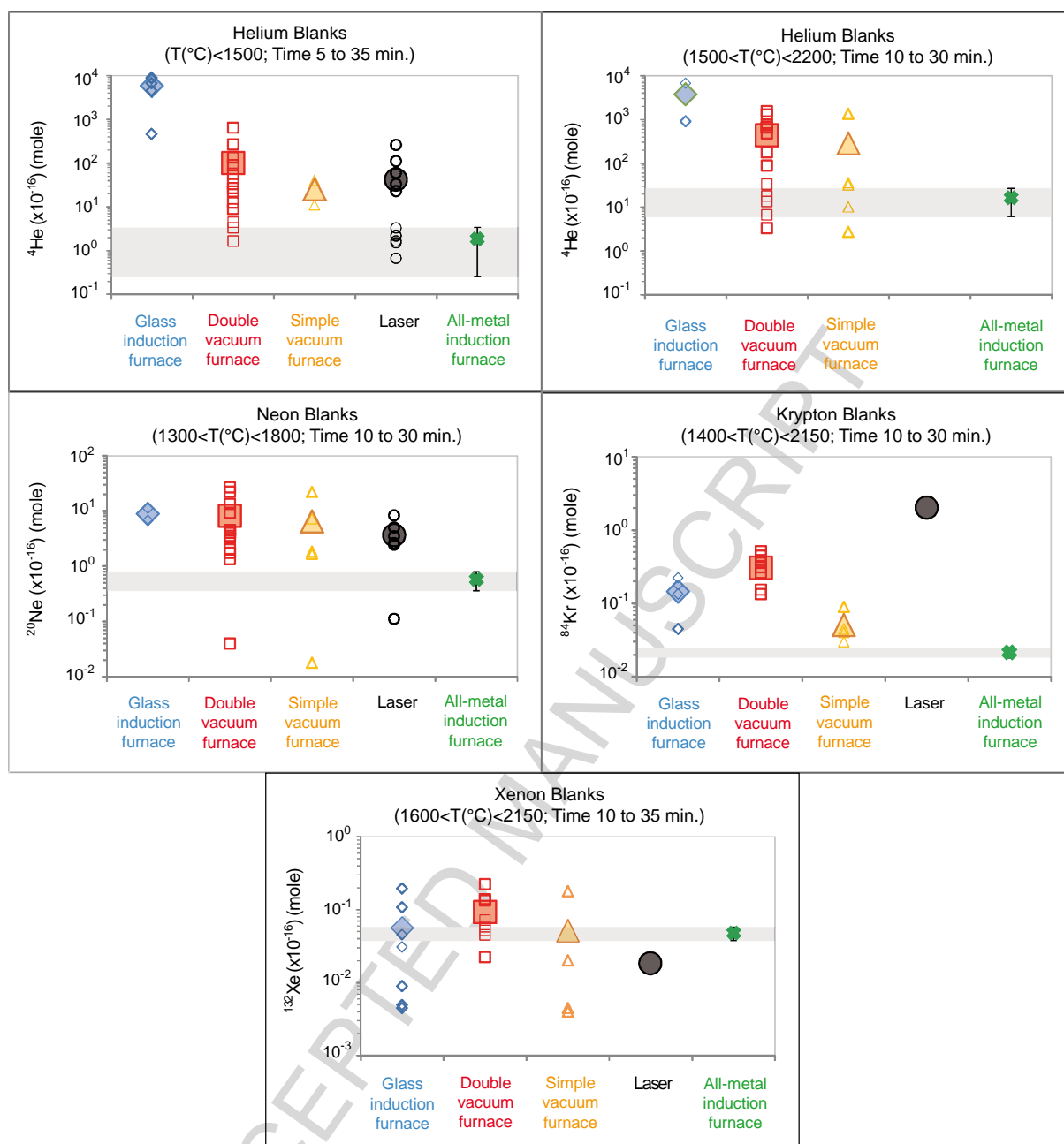


Figure 7: Summary of noble gas blanks measured with different heating methods: glass induction furnaces (blue diamonds); double vacuum resistance furnaces (red squares), simple vacuum resistance furnaces (yellow triangles), laser heating (black circles) and the all-metal induction furnace presented here (green cross). Large symbols represent the average blanks for each method. The all-metal induction

blanks were measured without metallic foil melting. Values and references are provided in Supplementary information, table 1.

#### 4 Noble gas extraction yields

The typical duration of the first sample heating tests was 10 to 20 minutes at  $\approx 1500^{\circ}\text{C}$  for Ne and at  $\geq 1700^{\circ}\text{C}$  for He, Kr and Xe.

Duplicate extractions indicated that helium was completely released from pyroxene and pyroxene-olivine by heating at  $1750^{\circ}\text{C}$  for 10 minutes. For refractory Mg-rich olivine, it is better to increase the temperature to  $1770^{\circ}\text{C}$  and the duration to 20 minutes in order to achieve complete extraction.

Neon is likewise fully (98-100%) released from quartz of different grain sizes at  $1500^{\circ}\text{C}$  for 20 minutes.

Xe and Kr analyses of barite ( $\text{BaSO}_4$ , dissociation at  $1600^{\circ}\text{C}$ ) and quartz ( $\text{SiO}_2$ , decrepitation of fluid inclusions at around  $1600^{\circ}\text{C}$ ) samples have also been conducted with this new furnace. These consisted of performing two extraction steps at  $800^{\circ}\text{C}$  and  $1700^{\circ}\text{C}$ , and an additional re-extraction at a similar or slightly higher temperature ( $1750^{\circ}\text{C}$ ). Overall, 90% of the gases were released during the first two steps, and 10% of the gases were extracted during the re-extraction step.

## 5 Conclusion

A new induction furnace has been developed for noble gas extraction under ultra-high vacuum. A coil placed inside an all-metal single vacuum chamber heats a crucible located in the same chamber by induction. The furnace is able to reach a temperature of at least 1800°C within only a few minutes (heating/cooling rates of about 400°C.min<sup>-1</sup>), thanks to its low thermal inertia and to its assemblage which prevents degradation by thermal shocks. The whole furnace and sample holder (carousel) can be baked at 200°C over several days. The vacuum vessel and upper/lower flanges are cooled by circulation of water in a double wall during heating, warranting low noble gas blanks compared to existing furnaces.

Future tests will focus on (i) testing new crucibles with low Ar blanks in order to be able to analyse this noble gas in geological samples, (ii) adding a thermocouple or a new optical pyrometer in order to obtain more rigorous control of the temperature, especially in the 100-900 °C temperature range, and (iii) testing Pt crucibles to enable us to quantitative extract nitrogen together with noble gases.

A patent for this new furnace has been deposited at the French Institut National de la Propriété Industrielle. Marketing of the furnace will be assured by the company Cryoscan (contact@cryoscan-uhv.com).

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## References

**Aciego S.M., DePaolo D.J., Kennedy B.M., Lamb M.P., Sims K.W.W. and Dietrich W.E. (2007)**

Combining [3He] cosmogenic dating with U-Th/He eruption ages using olivine in basalt. . Earth and Planetary Science Letters, **254**, 288-302

**Avice G., Meier M.M.M., Marty B., Wieler R., Kramers J.D., Langenhorst F., Cartigny P., Maden C., Zimmermann L., Andreoli M.A.G., (2015).**

A comprehensive study of noble gases and nitrogen in “Hypatia,” a diamond-rich pebble from SW Egypt. Earth and Planetary Science Letters, **432**, 243–253

**Ammon K., Dunai T.J., Stuart F.M., Meriaux A.-S. and Gayer E. (2009)**

Cosmogenic <sup>3</sup>He exposure ages and geochemistry of basalts from Ascension Island, Atlantic Ocean. Quaternary Geochronology, **4**, 525-532

**Becker R.H. and Pepin R.O. (1984)**

The case for a martian origin of the shergottites: nitrogen and noble gases in EETA 79001. Earth and Planetary Science Letters, **69**, 225-242

**Blard P.H., Pik R., Lavé J., Bourlès D., Burnard P.G., Yokochi R., Marty B. and Trusdell (2006)**

Cosmogenic <sup>3</sup>He production rates revisited from evidences of grain size dependent release of matrix-sited helium. Earth and Planetary Science Letters, **247**, 222-234

**Blard P.H. and Pik R. (2008)**

An alternative isochron method for measuring cosmogenic  $^3\text{He}$  in lava flows. Chemical Geology, **251**, 20-32

**Blard P.H., Balco G., Burnard P.G., Farley K.A., Fenton C.R., Friedrich R., Jull A.J.T., Niedermann S., Pik R., Schaefer J.M., Scott E.M., Shuster D.L., Stuart F.M., Stute M., Tibari B., Winckler G. and Zimmermann L. (2015)**

An inter-laboratory comparison of cosmogenic  $^3\text{He}$  and radiogenic  $^4\text{He}$  in the cronus-P pyroxene standard. Quaternary Geochronology, **26**, 11-19

**Burgess R., Cartigny P., Harrison D., Hobson E. and Harris J. (2009)**

Volatile composition of microinclusions in diamonds from the panda kimberlite, Canada: Implications for chemical and isotopic heterogeneity in the mantle. Geochimica et Cosmochimica Acta, **73**, 1779-1794

**Chennaoui-Aoudjehane H. (1992)**

Modélisation de la solubilité des gaz rares He, Ne, Ar, Kr et Xe dans les liquides silicatés à 1500°C. Thèse 138 p

**Chiggiato P., Benvenuti C., Canil G., Collin P., Cosso R., Guerin J. and Ilie S. (1999)**

Surface cleaning efficiency measurements for UHV applications. Vacuum, **53**, 317-320

**Farley K.A., Reiners P.W. and Nienow V. (1999)**

An apparatus for high-precision helium diffusion measurements from minerals. Analytical Chemistry, Technical notes, **71**, 2059-2061

**Farley K.A., Libarkin J., Mukhopadhyay S. and Amidon W. (2006)**

Cosmogenic and nucleogenic  $^3\text{He}$  in apatite, titanite, and zircon. Earth and Planetary Science Letters, **248**, 451-461

**Foeken J.P.T., Stuart F.M., Dobson K.J., Persano C. and Vilbert D. (2006)**

A diode laser system for heating minerals for (U-Th)/He chronometry. Geochemistry Geophysics Geosystems, Technical brief, **7**, Q04015

**Foeken J.P.T., Day S. and Stuart F.M. (2009)**

Cosmogenic  $^3\text{He}$  exposure dating of the quaternary basalt from Fogo, Cape Verde: Implications for tectonic zone and magmatic reorganisation. Quaternary Geochronology, **4**, 37-49

**Füri E., Aléon-Toppani A., Marty B., Libourel G. and Zimmermann L. (2013)**

Effects of atmospheric entry heating on the noble gas and nitrogen content of micrometeorites. Earth and Planetary Science Letters, **377-378**, 1-12

**Füri E., Chaussidon M. and Marty B. (2015)**

Evidence for an early nitrogen isotopic evolution in the solar nebula from volatile analyses of a CAI from the CV3 chondrite NWA 8616. Geochimica et Cosmochimica Acta, **153**, 183-201

**Honda M., Reynolds J.H., Roedder E. and Epstein S. (1987)**

Noble gases in diamonds: Occurrences of solarlike helium and neon. *Journal of Geophysical Research*, **92**, N°B12, 12.507-12521

**Honda M., Mcdougall I, Patterson D.B., Doulgeris A. and Clague D.A. (1993)**

Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: A solar component in the Earth. *Geochimica et Cosmochimica Acta*, **57**, 859-874

**Jambon A., Weber H. and Braun O. (1986)**

Solubility of He, Ne, Ar, Kr and Xe in a basalt melt in the range 1250-1600°C. Geochemical implications. *Geochimica et Cosmochimica Acta*, **50**, 401-408

**Johnson L.H., Burgess R., Turner G., Milledge H.J. and Harris J.W. (2000)**

Noble gas and halogen geochemistry of mantle fluids: Comparison of african and canadian diamonds. *Geochimica et Cosmochimica Acta*, **64**, 717-732

**Kurz M. (1986)**

In situ production of terrestrial cosmogenic helium and some application to geochronology. *Geochimica et Cosmochimica Acta*, **50**, 2855-2862

**Lavielle B., Marti K., Jeannot J.P., Nishiizumi K. and Caffee M. (1999)**

The  $^{36}\text{Cl}$ - $^{36}\text{Ar}$ - $^{40}\text{K}$ - $^{41}\text{K}$  records and cosmoc ray production rates in iron meteorites. *Earth and Planetary Science Letters*, **170**, 93-104

**Marty B, Lenoble M. and Vassard N. (1995)**

Nitrogen, helium and argon in basalt: a static mass spectrometry study. Chemical Geology (Isotope Geoscience Section), **120**, 183-195

**Maruoka T. and Matsuda J. (2001)**

New crucible for noble gas extraction. Chemical Geology, **175**, 751-756

**Moreira M. and Allègre C.J. (2002)**

Rare gas systematics on Mid Atlantic Ridge (37-40°N). Earth and Planetary Science Letters, **198**, 401-416

**Nichols R. H. Jr., Hohenberg C.M. and Olinger C.T. (1994)**

Implanted solar helium, neon, and argon in individual lunar ilmenite grains: Surface effects and a temporal variation in the solar wind composition. Geochimica et Cosmochimica Acta, **58**, 1031-1042

**Niedermann S., Bach W. and Erzinger J. (1997)**

Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: Decoupling of helium and neon isotope systematics. Geochimica et Cosmochimica Acta, **61**, 2697-2715

**Ott U. (1988)**

Noble gases in SNC meteorites: Shergotty, Nakhla, Chassigny. Geochimica et Cosmochimica Acta, **52**, 1937-1948

**Persano C., Stuart F.M., Bishop P. and Barfod D.N. (2002)**

Apatite (U-Th)/He age constraints on the development of the great escarpment on the southeastern Australian passive margin. *Earth and Planetary Science Letters*, **200**, 79-90

**Pi T., Solé J. and Taran Y. (2005)**

(U-Th)/He dating of fluorite: application to the La Azul fluor spar deposit in the Taxco mining district, Mexico. *Mineralium Deposita*, **39**, 976-982

**Pujol M., Marty B., Burnard P., Philippot P., 2009.**

Xenon in Archean barite: Weak decay of  $^{130}\text{Ba}$ , mass-dependent isotopic fractionation and implication for barite formation. *Geochimica et Cosmochimica Acta* **73**, 6834–6846.

**Staudacher Th, Jessberger E.K., Dörflinger D. and Kiko J. (1978)**

A refined ultrahigh-vacuum furnace for rare gas analysis. *J. Phys. E: Sci. Instrum*, **11**, 781-784

**Stuart F.M., Harrop P.J., Knott S. and Turner G. (1999)**

Laser extraction of helium isotopes from Antarctic micrometeorites: Source of He and implications for the flux of extraterrestrial  $^3\text{He}$  to earth. *Geochimica et Cosmochimica Acta*, **63**, 2653-2665

**Sumino H., Dobrzhinetskaya L.F., Burgess R. and Kagi H. (2011)**

Deep-mantle-derived noble gases in metamorphic diamonds from the Kokchetav massif, Kazakhstan. *Earth and Planetary Science Letters*, **307**, 439-449

**Takaoka N. (1976)**

A low blank, metal system for rare gas analysis. *Mass spectrometry*, **24(1)**, 73-86

**Vermeesch P., Balco G., Blard P. H., Dunai T. J., Kober F., Niedermann S., Shuster D. L., Strasky S., Stuart F. M., Wieler R. and Zimmermann L. (2015)**

Interlaboratory comparison of cosmogenic  $^{21}\text{Ne}$  in quartz. *Quaternary Geochronology*, **26**, 20-28

**Williams A.J., Stuart F.M., Day S.J. and Phillips W.M. (2005)**

Using pyroxene microphenocrysts to determine cosmogenic  $^3\text{He}$  concentrations in old volcanic rocks; an example of landscape development in central Gran Canaria. *Quaternary Science Reviews*, **24**, 211-222

**Zimmermann L., Blard P.H., Burnard P., Medynski S., Pik R., and Puchol N. (2012)**

A new single vacuum furnace design for cosmogenic  $^3\text{He}$  dating. *Geostandards and Geoanalytical Research*, **36(2)**, 121-129